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PRELIMINARY COMMUNICATIONS

Liquid crystalline phase transitions for 4,4‴-dialkyloxyquaterphenyl homologues

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The liquid crystalline phase transitions of a homologous series of 4,4‴-dialkyloxyquaterphenyls (DAQP) have been studied by differential scanning calorimetry and optical microscopy. The DAQP homologues, for which the number of carbon atoms in the alkyloxy group (n) is 5–9, show a S_A phase, while the higher homologues (n=9–12, 18) show a S_C phase.

As is well known, biphenyl derivatives have stood in the spotlight as the most important and popular liquid crystalline compounds, but not much attention has been paid to the liquid crystalline properties of higher polyphenyl derivatives. To date, mesogenic properties of quaterphenyl derivatives have been studied by only a few researchers [1–5]. Vorländer [1] first reported that 4,4‴-diaminoquaterphenyl and 4,4‴-dinitroquaterphenyl exhibited a mesomorphic phase. Schubert *et al.* [3], found smectic C (S_C) and nematic phases in 4,4‴-di-*n*-acylquaterphenyls and a smectic phase in 4,4‴-di-*n*-alkylquaterphenyls, dialkylquaterphenyl-4,4‴-dicarboxylates and 4,4‴-bis-(5-*n*-alkyloxycarbonylpentyl)quaterphenyls. Also, Chan *et al.* [5], established the mesomorphic properties of a few difluorinated 4,4‴-dialkyl- and -dialkoxyquaterphenyls obtained as by-products from certain coupling reactions, but the liquid crystal behaviour of the simpler 4,4‴-dialkyloxyquaterphenyls (hereafter DAQP) has not been studied to our knowledge. In this paper, we report the mesomorphic properties of a homologous series of thirteen DAQP (with carbon numbers in the alkyloxy group (n) of 1–12 and 18).

DAQP-homologues were synthesized by a debromination reaction from 4-bromo-4′-alkyloxybiphenyl: 4-bromo-4′-alkyloxybiphenyl (6·7 g, 0·02 mol), 4M-aqueous KOH (10 ml) and 5 per cent Pd-C (0·9 g) were added to ethylene glycol (80 ml)/water (10 ml) and the solution was stirred at 110°C for 48 h. After adding water (200 ml), the reaction mixture was neutralized by HCl and the Pd–C residue was removed by dissolving the organic product in hot DMF (500 ml). The crude products were purified by recrystallizations from DMF for the n = 1–3 homologues and from toluene for the n=4–12 and 18 homologues, giving colourless crystals (yield: 10–20 per cent). The

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products were identified as the required materials and judged to be fully pure by elementary analyses, IR spectroscopy and MS. Elementary analytical results for C and H coincided with the calculated values within 0·3 per cent for all homologues. IR(KBr): 3038, 2955, 2922, 2873, 2857, 1256, 1028, 811 cm^{-1}. MS: *m/e*, 506, 422, 338 for the $n=6$ compound.

Thermal properties were determined by differential scanning calorimetry (Seiko-Denshi Co., SSC-5000) at a heating/cooling rate of 5 K min^{-1}. Texture observations for the mesophases were performed by optical polarizing microscopy (Olympus BH-2 in conjunction with a Linkam TH-600 RMS hot stage) at a heating/cooling rate of 5 K min^{-1}.

Phase transition temperatures and entropy changes for the DAQP homologues are listed in the table. All DAQP compounds show a number of crystal–crystal phase transitions. Plots of the mesomorphic phase transition temperature versus the carbon numbers of the alkyloxy group (n) are shown for the DAQP homologues in the figure. The $n=1$–4 compounds have high melting points (T_m) above 603 K and sublimed so rapidly just above T_m that the mesomorphic phase could not be determined. The $n=5$–9 compounds show a smectic A (S_A) phase with a focal-conic texture on heating and a fan texture on cooling—both readily observed using crossed polarizers. The $n=9$–12 and 18 compounds have a smectic C (S_C) phase; the S_C phase was identified by the simultaneous appearance of a broken-fan texture and a schlieren texture visible using crossed polarizers on cooling.

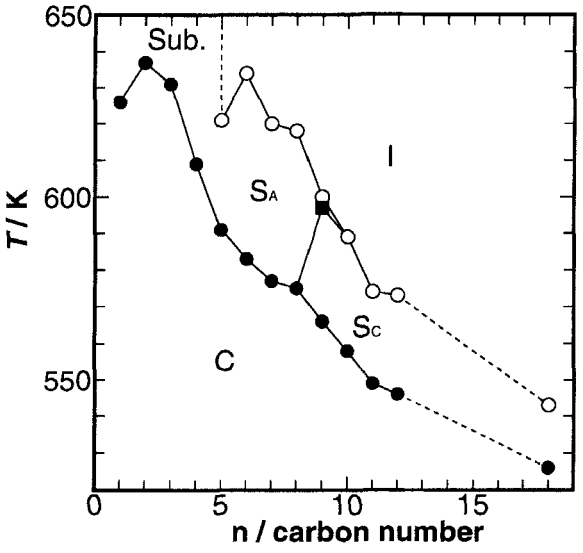
Consequently, the DAQP series shows S_A phases when n is between 5 and 8, both S_A and S_C phases when $n=9$, and S_C phases when $n>9$. It is noted that the clearing points (T_C) of the smectic A and C phases lie in the very high temperature range from 540 to 640 K, as a consequence of the long, rod-like, rigid core of quaterphenyl. As n increases, T_C gradually decreases, with an odd–even effect, over the S_A and S_C phases, and this means that the terminal group, in this case the alkyloxy group, influences the molecular packing in smectic A and C phases even when the central group consists of the long, rod-like, rigid quaterphenyl moiety.

Biphenyl derivatives usually show mesophases at low temperatures; for example, a smectic phase between 341 and 357 K for 4-hexyl-4′-hexyloxybiphenyl [6], while

Phase transition temperatures (K)/entropy changes ($JK^{-1}mol^{-1}$) for DAQP homologues.

n	C_1	C_2	C_3	C_4	S_C	S_A	I
1	● 604/17	● 626/21	● —	— —	— —	— †	—
2	● 548/16	● 637/16	● —	— —	— —	— †	—
3	● 529/16	● 631/16	● —	— —	— —	— †	—
4	● 520/17	● 544/1	● 609/17	● —	— —	— †	—
5	● 337/21	● 495/12	● 531/11	● —	— 591/16	● 621/5	●
6	● 341/11	● 477/11	● 521/1	● —	— 583/18	● 634/13	●
7	● 377/45	● 460/31	● 513/2	● —	— 577/21	● 620/15	●
8	● 356/8	● 482/8	● —	— —	— 575/23	● 618/18	●
9	● 396/57	● 439/5	● 453/14	● 566/22	● 597/3	● 600/15	●
10	● 397/53	● 433/13	● 449/14	● 558/23	● —	— 589/22	●
11	● 410/70	● 428/12	● 448/23	● 549/18	● —	— 574/12	●
12	● 406/66	● 423/15	● 447/12	● 546/25	● —	— 573/25	●
18	● 404/65	● 466/8	● —	— 526/30	● —	— 543/26	●

† Could not be determined due to sublimation of the sample.



Phase transition temperatures (T) versus the number of carbon atoms in the alkyloxy group (n) for 4,4‴-dialkyloxyquaterphenyl homologues. ●, melting point; ○, clearing point; ■, smectic C (S_C)–smectic A (S_A) transition. C, crystal; I, isotropic liquid; Sub., sublimation.

terphenyl derivatives show much higher temperature mesophases, for example, a smectic phase between 466 and 491 K for 4,4″-dihexylterphenyl [7]. Unexpectedly, the mesomorphic properties have not been studied for 4,4′-dialkyloxybiphenyls and 4,4″-dialkyloxyterphenyls, except for 4,4″-dimethoxyterphenyl, which shows a smectic phase between 532 and 540 K and a nematic phase between 540 and 541 K [8]; a number of fluorinated 4,4″-di-*n*-alkyloxyterphenyls have also been studied [5]. With polyphenyl constituting the central group, the molecular core is longer, and the thermal stabilities of the mesophases are certainly enhanced. It would be of interest to study the contribution of extended lengths of polyphenyl to the thermal stabilities of mesophases.

In conclusion, we report that DAQPs show a S_A phase in the $n = 5$–9 range and a S_C phase in the $n = 9$–12 and 18 range, both with very good thermal stability. Further studies on the mesomorphic properties of quaterphenyl derivatives are progressing in our laboratories.

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